Reactive Extraction of Propionic Acid Using Tri-*N*-butyl Phosphate in Petroleum Ether: Equilibrium Study

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In present paper, the recovery of propionic acid from aqueous phase by reactive extraction was studied using tri-*n*-butyl phosphate (TBP) in petroleum ether. Extraction using pure diluent was found to be poor. Using the mixture of extractant-diluent the extraction was significantly improved. Results were presented in terms of distribution coefficient, equilibrium complexation constant, loading ratio and extraction efficiency. Propionic acid and TBP were found to form (γ = 1:1) complex with no overloading.

Key words:
Propionic acid, reactive extraction, TBP, petroleum ether, liquid-liquid equilibrium

Introduction

Propionic acid is an important carboxylic acid used primarily for animal feed preservation, in human foods, mainly in baked goods and cheese, manufacture of antiarthritic drugs, perfumes and flavors, plasticizers, mould preventives in silage and hay, and as a solvent.[1] Propionic acid is industrially produced by the petrochemical route.[2] However, with the increase in the prices of petrochemical products, alternative means of propionic acid production have been investigated. Fermentation technology emerges as the best alternative providing the advantage of being energy efficient. Extractive fermentation provides the advantages of increased reactor productivity, production and recovery of the fermentation product in one continuous step, and reduction in downstream processing load and recovery cost.[3]

A lot of work has been done on the reactive extraction of different carboxylic acids using organophosphorous, tertiary and quaternary amine.[4–15] TBP is an organophosphorous extractant and very little work can be found on the recovery/removal of propionic acid using it.[16–20] In view of this, attempts were made to study the extraction of propionic acid using TBP in petroleum ether. The data on the distribution coefficient, equilibrium complexation constant, loading ratio and extraction efficiency are presented.

Theory

Strongly solvating extractants like organophosphorous compounds have primarily been used in inorganic analysis for the extraction and separation of inorganic acids or metal species.[21] Since phosphoryl can form hydrogen bonds to proton donors, strongly solvating extractants can also be used for the extraction of acidic organic compounds. Weak organic acids are extracted by organophosphorous compounds with a significantly higher distribution ratio. The high polarity of the phosphoryl group in tributyl phosphate (TBP) enables it to act as a strong Lewis base.[22]

The recovery of propionic acid using TBP is by the formation of a complex via the interfacial reaction and can be represented as:[23,24]

$$HA_{aq} + pS_{org} \rightleftharpoons (HA.S_p)_{org} \quad (1)$$

As the propionic acid-TBP complex is formed it is rapidly extracted into the organic phase. The equilibrium complexation constant is defined as:

$$K_S = \frac{[HA.S_p]_{org}}{[HA]_{aq}[S]^p_{org}} \quad (2)$$

K_S is expected to depend on the properties of the acid and the solvation efficiency of the diluent used. The experimentally accessible distribution ratio K_D is given as:

$$K_D = \frac{[HA]_{org}}{[HA]_{aq}} = \frac{[HA.S_p]_{org}}{[HA]_{aq} + [A^-]_{aq}} \quad (3)$$

It is well known that propionic acid dissociates in aqueous solution and dimerizes in a non-polar solvent. The dissociation of the acid in the aqueous phase is given as:

$$HA \rightleftharpoons H^+ + A^- \quad (4)$$

$$K_{HA} = \frac{[H^+][A^-]}{[HA]} \quad (5)$$

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From (3) and (5)

$$K_D = \frac{K_S [HA]_{aq} [S]_{org}^p}{[HA]_{aq} + K_{HA} [HA]_{aq} / [H^+]_{aq}} = \\ = \frac{K_S [S]_{org}^p}{1 + K_{HA} / [H^+]_{aq}} \quad (6)$$

$[S]_{org}$ can be expressed as

$$[S]_{org} = [S]_{org}^{initial} - p[HA]_{org} \quad (7)$$

Further, if $[H^+] / K_{HA}$ is very small (since dilute concentrations of propionic acids are taken), eq. (6) can be written as

$$\log(K_D) = \log(K_S) + p \log[S]_{org} \quad (8)$$

Thus, the plot of $\log(K_D)$ versus $\log[S]_{org}$ would yield a straight line with the slope of p and the intercept of $\log(K_S)$, from where K_S can be obtained.

Eqs. (1) and (4) are a simplified, though realistic, version of a more general and thermodynamically strict one that includes activity coefficient and/or allows for the simultaneous formation of two, or perhaps three, different solvates, depending on the organic phase loading.[25] When there is stoichiometric deficiency of the solvating agent S in the system, the distribution ratio (eq. (6)) requires the addition of appropriate terms to account for the acid extraction by the diluent alone and its dimerization. King *et al.*[4] have investigated extensively the evaluation of the eq. (8) and found the constants of the equation. The solvation number (p) of the acid was found to be the same as the number of –COOH group in the acid molecule. Propionic acid contains one –COOH group and thus the solvation number (p) can be assumed to be unity.

The extent to which the organic phase can be loaded with propionic acid is expressed as the overall loading factor (Z_t) as,

$$Z_t = \frac{[HA]_{org}}{[S]_{org}^{initial}} \quad (10)$$

and is dependent on the extractability of the acid (strength of acid base interaction) and its aqueous phase concentration. The degree of extraction is defined as the ratio of propionic acid concentration in organic phase to the sum of acid concentration in organic and aqueous phase and is defined in terms of K_D as

$$E\,\% = \frac{K_D \cdot 100}{1 + K_D}. \quad (11)$$

Experimental

Materials

TBP (Himedia, India), a phosphorous bonded oxygen donor, is a light colorless liquid with molecular mass of M_r = 266.32 and density of ρ = 0.92 g cm^{-3}. Propionic acid (99 %) (Himedia, India) and petroleum ether (s. d. fine chem. Ltd, Mumbai, India) were of technical grade and were used without pretreatment. Distilled water was used to prepare the solutions of various concentrations of propionic acid. NaOH used for titration was of analytical grade and was supplied by Ranbaxy, India. For the standardization of NaOH, oxalic acid (99.8 %) was obtained from s. d. fine chem. Ltd., India. Phenolphthalein solution (pH range 8.2–10.0) was used as indicator for titration and obtained from Ranbaxy, India. The range of pH of initial propionic acid solution for the experiment was 2.65–3.14 at room temperature. The initial TBP concentrations in the range of c = 0.37–1.65 kmol m^{-3} (10–40 %) and the initial aqueous acid concentrations range of c = 0.05–0.4 kmol m^{-3} were used. Low concentration was used because propionic acid concentration in the fermentation broth is not greater than c = 0.5 kmol m^{-3}.[26]

Methods

The extraction experiments were performed using a temperature controlled water bath shaker at room temperature (T = 305 K). Equal volumes (25 cm^{-3}) of aqueous and organic phases were shaken for 12 h and then left to settle for at least 2 h at a fixed temperature (305 K) and atmospheric pressure (p = 101.2 kPa).[4] Aqueous phase pH was measured by an Orion 3 star pH Benchtop (Thermo Electro Corporation). Aqueous phase acid concentration was determined by titration with NaOH and by HPLC. HPLC system (WATERS 1523) was composed of binary pump, refractive index detector (WATERS 2414) and dual λ absorbance detector (WATERS 2487). The column used was C-18. Results by both methods (titration and HPLC) were found to be comparable. The acid content in the organic phase was determined with a mass balance.

Results and discussion

The extraction equilibria of propionic acid by petroleum ether (physical) and TBP-petroleum ether combination (chemical) were studied. The physical and chemical equilibria are shown in Fig. 1. The extraction with only petroleum ether was low with the K_D value of 0.25. The reason for the poor extraction by petroleum ether is the higher affinity of propionic acid for water than petroleum

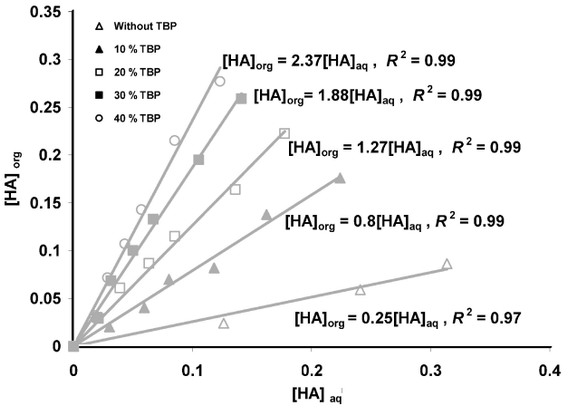

Fig. 1 – *Equilibria for extraction of propionic acid in petroleum ether with and without TBP*

ether. Further, solvent extraction with conventional solvents require very high solvent flow rates and this results in substantial dilution of acid and increases the further processing cost.[27]

TBP, an organophosphorous compound, contains a phosphoryl group which is a stronger lewis base than carbonyl one. This leads to high distribution coefficient. TBP was selected because of low water co-extraction (w = 4.67 %) and very low solubility in aqueous phase (w = 0.039 %). TBP contains =P–(O)–OH group, which has a marked tendency toward intermolecular hydrogen bonding. Due to the presence of both electron donor and electron acceptor groups in =P–(O)–OH grouping, it undergoes specific interactions like self-association and molecular complex formation with diluents or other solutes. The knowledge of these factors is necessary for understanding the mechanism of extraction, the effect of diluents and role of additional reagents.

Since TBP has a relatively high viscosity (η = $3.56 \cdot 10^{-3}$ Pa s) and specific gravity close to unity (0.98), it is used along with low viscosity and low density diluents, which could facilitate good phase separation in continuous extraction process. Therefore, petroleum ether was used as diluent. It can be seen that the extraction using TBP in petroleum ether is much higher than using petroleum ether alone. The distribution coefficients for 10 %, 20 %, 30 % and 40 % TBP are K_D = 0.8, 1.27, 1.88 and 2.37 respectively.

Table 1 demonstrates the influence of the organic solvent and the organic phase concentration of TBP on the distribution coefficient of propionic acid. TBP concentration was varied from 10 – 40 % (c = 0.37 – 1.65 kmol m^{-3}) in petroleum ether for the acid concentrations of c = 0.05 – 0.4 kmol m^{-3}. Usually, TBP fraction was not used above x = 40 % because of the viscosity problem previously mentioned. Zhong *et al.*[28] found that the maximum K_D values were found for the extractant concentration of 20–40 %.

Table 1 – *Extraction equilibrium results for TBP/petroleum ether/propionic acid system at 305 K for the various concentrations of TBP and acid*

Initial PA conc. c/kmol m^{-3}	Solvent conc. c/kmol m^{-3}	pH_{eq}	K_D	E/%	Z_t
0.05	0.37	3.27	0.667	40.00	0.054
	0.74	3.37	1.381	58.00	0.039
	1.10	3.39	1.564	61.00	0.028
	1.65	3.41	1.778	64.00	0.019
0.1	0.37	3.09	0.681	40.51	0.109
	0.74	3.20	1.564	61.00	0.082
	1.10	3.26	2.175	68.50	0.062
	1.65	3.28	2.509	71.50	0.043
0.15	0.37	3.02	0.875	46.67	0.189
	0.74	3.07	1.362	57.66	0.117
	1.10	3.14	2.000	66.67	0.091
	1.65	3.18	2.488	71.33	0.065
0.2	0.37	2.93	0.695	41.00	0.222
	0.74	3.01	1.353	57.50	0.155
	1.10	3.07	1.985	66.50	0.121
	1.65	3.11	2.509	71.50	0.087
0.3	0.37	2.85	0.852	46.00	0.373
	0.74	2.89	1.206	54.67	0.222
	1.10	2.96	1.857	65.00	0.177
	1.65	3.01	2.529	71.66	0.168
0.4	0.37	2.78	0.786	44.01	0.476
	0.74	2.83	1.254	55.63	0.301
	1.10	2.89	1.837	64.75	0.235
	1.65	2.92	2.252	69.25	0.168

The study showed that the loading ratio was independent of the TBP fraction in petroleum ether. Thus, for non-aggregating systems in inert diluents (alkanes or aromatic diluents), there was no effect of the TBP fraction on loading ratio and (γ = 1:1) TBP-acid complex formation could be assumed. This was also verified by the plot of $\log(K_D)$ against $\log[B]_{org}$ according to eq. (8) in which the slope of unity was obtained (Fig. 2).

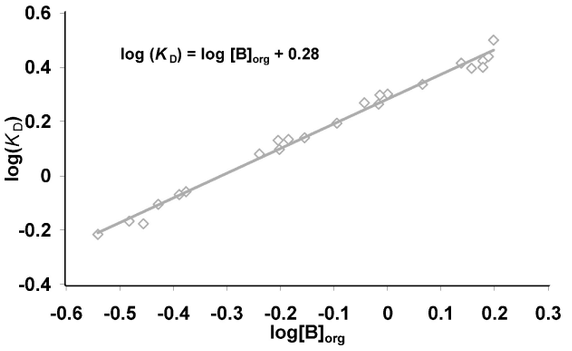

Fig. 2 – *Distribution coefficient of propionic acid in TBP dissolved in petroleum ether as the function of free TBP concentration in the organic phase*

The equilibrium complexation constants for the extraction using TBP in petroleum ether and that found in literature are listed in Table 2. The comparison clearly shows that TBP with petroleum ether shows improved extraction and is suited to be a better extractant-diluent combination.

Table 2 – *Equilibrium complexation constants for extraction of propionic acid using various extractant-diluent combinations*

Extractant	Diluent	Extractant concentration c/kmol m^{-3}	K_S/ m^3 kmol^{-1}	Reference
TBP	petroleum ether	0.37–1.65	1.91	Present work
Amberlite LA-2	hexane	0.04–0.21	1.51	12
TOA	heptane	0.92	1.43	31
TOA	xylene	0.92	0.51	31
TOA	MIBK	0.92	1.91	31

Different approaches have been used to quantify the effect of diluents on the (γ = 1:1) complexation. Both partition and self-association constants are strongly dependent on the nature of the diluents; i.e. the thermodynamic activity of the species taking part in the organic phase equilibria changes when one diluent is replaced with the other. The effect of diluent on partition and self-association constants was explained by specific interactions only between TBP and the diluent. King *et al.*[29] have suggested the use of Hildeband solubility parameter as the measure of solvation of the complex by the diluent.

The extraction constant has been correlated with solvation energy: 'inert' the solvent, the smaller is the extraction constant; which frequently occurs in solvent extraction practice. The effect of the diluents is determined by the ratio of contributions of solvation of extractant and the extracted complex to the free energy of extraction. Solvation, in turn, depends on different kinds of intermolecular forces which cannot be determined merely by the physical parameters like boiling point, dipole moment, dielectric constant, etc. However, in some cases solvation energy is represented in terms of empirical parameters of solvent polarity. The parameters most frequently used are Z parameter (proposed by Kosower[30]) which account for the influence of the solvent on the position of the charge transfer band in the spectrum of alkylpyridine iodide, and the E_T parameter which is based on the absorption spectrum of pyridinium-*n*-phenol-betaine. The greater the E_T and Z values, the greater the solvating power of solvent.

Conclusion

Reactive extraction is one of the alternatives to conventional process for removal of carboxylic acids from fermentation broths and waste streams. Recovery of propionic acid by reactive extraction using tri-*n*-butyl phosphate (TBP) in petroleum ether was studied. TBP is a strong solvating extractant, containing a phosphoryl group whose high polarity enables it to act as a strong lewis base and, as a result, it can form acid base complex when contacted with propionic acid. Extraction by petroleum ether alone results in very low distribution coefficient. Therefore, it was proposed to use TBP with petroleum ether. The extraction using TBP (10–40 %) in petroleum ether was found to be much higher, and was found to increase with increasing TBP in petroleum ether. The degree of extraction and loading ratio was calculated. The degree of extraction was found to increase with increase in TBP concentration. Loading ratios in all cases were less than 0.5, thus only (γ = 1:1) propionic acid–TBP complexes formed, with no overloading in any case. Equilibrium complexation constant was predicted at K_S = 1.91 m^3 kmol^{-1}.

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Nomenclature

c – concentration, kmol m^{-3}
K_D – distribution coefficient, –
K_S – extraction equilibrium constant, m^3 kmol^{-1}
[HA] – concentration of acid, kmol m^{-3}
[S] – concentration of extractants, kmol m^{-3}
[HA.S] – concentration of acid-extractant complex, kmol m^{-3}
[H^+] – concentration of proton, kmol m^{-3}
[A^-] – concentration of anion, kmol m^{-3}
K_{HA} – dissociation constant of propionic acid (pK_{HA} = 4.67), m^3 kmol^{-1}
E – degree of extraction, –
Z_t – loading ratio,
M_r – relative molar mass
T – temperature, K
ρ – density, g cm^{-3}
p – pressure, kPa
η – viscosity, Pa s
γ – mole ratio
w – mass fraction, %

Subscripts

aq – aqueous phase
org – organic phase
p – solvation number of TBP

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